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Automated SEM-EDS pottery classification based on minero-chemical quantitative parameters: an application on ancient Greek pottery from Adrano (NE Sicily, Italy)

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Abstract

A new SEM-EDS procedure for ancient ceramic classification, based on the automated acquisition and the semi-automated processing of multi-elemental X-ray maps, is described. Based on the detection of each aplastic inclusion, the procedure allows to simultaneously obtain a quantitative evaluation of both the inclusion mineral-chemical composition and the ceramic matrix chemical composition. The two datasets can individually or jointly be subjected to statistical methods. The proposed protocol was applied on a set of 22 samples of black glaze pottery from Adrano (North-Eastern Sicily), Hellenistic Age (4^{th} to 2^{nd} centuries B.C.). Two main groups emerged from the application of the procedure, mainly distinguished for their quartz-feldspars vs calcium-aluminosilicate relative abundance as the inclusion mineral-chemical composition is concerned and for their matrix SiO_2 vs CaO. The classification based on the inclusion mineral-chemical data obtained with the proposed method mirrors the results from the traditional OM observation, but when the two data sets are simultaneously considered a subtler differentiation is observed, with the separation of one of the groups in two subgroups, allowing to refine the partition.

Key words: SEM-EDS, mineral-chemical analysis, black glaze pottery, Adrano, X-Ray mapping

1. Introduction

From an archaeological and historical point of view, ceramics are an extremely diffuse and durable material and represent a rich source of information on past civilizations and allow to reconstruct the organisation and technological level of the pottery workshops, the availability of the raw materials and the evolution of trade relationships [1], [2]. From an archaeometric point of view *fabrics* (defined as "the arrangement, size, shape, frequency and composition of ceramic material constituents", [3]) classification and characterization are fundamental to detect and document archaeologically meaningful compositional patterning within ancient ceramic assemblages [1], [4] and to provide relevant data, among other aspects, on ceramics production both from technological and social points of view. Alongside the macroscopic examination of the pottery paste, the petrographic analysis performed by optical microscopy (OM) is the classical archaeometric method to define *fabrics* [1], [4], [5], allowing to obtain both the mineralogical composition and the morphological features of the aplastic inclusions. This procedure can be performed following a semi-quantitative or even quantitative approach by means of the point-counting method that, on the other hand, is rather time consuming for the operator and therefore hardly applicable on large sets of samples [6, p. 598]. Thus, the OM examination results are often non-quantitative or semi-quantitative, allowing identifying significant *fabric* differences, but preventing a finer classification. Moreover, petrographic analysis may be performed by scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectrometry (EDS) that, despite a loss of overall information with respect to the OM, allows obtaining the chemical composition of the inclusions [5], [7]–[10], together with the chemical analysis of the clay matrix by spot or small inclusion-free raster areas examination. Besides the typical operator-controlled SEM-EDS application, several computer-controlled procedures were proposed, mainly for image analysis and automated mineral analysis. These methods are either based on the inclusion identification from the backscattered (BS) electrons image coupled with their EDS analysis in their geometric centre or in different points [11], [12] or consist of spot analyses collected along a predefined grid using an automated stage or the remote scanning of the electron beam, followed by *a posteriori* image reconstruction. The QEMSCAN system developed by CSIRO [13] is based on the acquisition of a grid of spot spectra, at intervals between 5 and 20 μm [14] and each analysis is compared to a mineral formula. It was applied in different fields, from the mining industry to archaeology [14]–[17].

A common shortcoming of these acquisition techniques is the processing of the obtained image. In fact, spot spectra grid often does not have sufficient spatial resolution to allow a good morphological processing. Regarding the BS images, they often suffer from a contrast insufficient to generate multimodal histograms. A general review on multivariate statistical methods to process

images is reported in Bonnet [18].

In the present work a new protocol is presented, in order to perform a SEM-EDS semi-automated quantitative simultaneous evaluation of the mineral-chemical composition of the inclusions and of the chemical composition of the ceramic matrix, i.e. inclusions coarser or finer of 15 μm, respectively [19], based on the acquisition of X-ray spectrum images. Each inclusion is outlined by using thresholds on each map obtained from the X-ray spectrum images. Summing the spectra of all the inclusion points, the inclusion average composition is calculated, with greater precision with respect to elemental X-ray maps, due to the high signal-to-noise ratio (S/N), together with a spatial resolution improved by one order of magnitude with respect to the grid-based acquisition.

Matrix chemical composition is determined using the sum spectrum of the whole map area not associated to inclusions or pores.

The proposed method allows to automatically (without an operator presence) and simultaneously obtaining with a single 4-hours analysis both the inclusion mineral-chemical composition and normative distribution and the matrix chemical profile, together with different morphometric parameters. This whole data set represents a very efficient tool to obtain the *fabrics* classification of a certain *corpus* of ceramic materials. Moreover, when adequate reference materials are available, the inclusion petrographic and morphometric profile might also be used for a provenance evaluation [19]. Indeed, the overall quantitative results allow applying statistical methods on both the mineral-chemical (inclusions) and the chemical (matrix) datasets, in order to perform reliable *fabric* partition. Moreover, the procedure allows the acquisition of morphometric data potentially useful for the *fabrics* classification.

The procedure was tested on a set of archaeological samples coming from the site of Adrano (northeastern Sicily, Southern Italy) with the aim of evaluating the method reliability.

2. Archaeological overview and sample description

Old Adranon (modern Adrano) is located on the south-western slope of Mount Etna, around 28 km from Catania, near the Simeto river (Figure 1SM). The area was inhabited from the Neolithic and in Hellenistic age the tyrant *Dionigi il Vecchio di Siracusa* established the Greek settlement to strengthen the Syracusan hegemony against, above all, the Carthaginians [20, XIV]. The settlement was probably a military base later converted into an urban centre, characterized by a regular road system and significant private houses [21]–[23]. Public buildings have not been recovered, while the massive defensive system surrounding the city is worth mentioning [23]. Necropolis areas were explored both in the western and in the eastern part of the city [22]. The presence of local ceramic workshops in Adrano was already suggested [24] both for the figured ceramic production

ascribable, for instance, to the artisans of the so-called *Gruppo di Adrano* [25] and for the discovery of kiln wastes in the site [23]. These observations strengthen the theory of a vast local ceramic manufacture, both a daily use limited quality pottery (black glaze) and figured and overglaze painted productions.

The 22 examined ceramic fragments come from the residential contexts. They were excavated in the first half of the 1980s, are datable from the second half of the 4th century B.C. to the end of the 2nd century B.C and belong to the black glaze production. This manufacture is characterized by a quite rough and not well-finished style, typical for all the Sicilian productions and especially from the second half of the 3rd century B.C. The slips are irregular, with recurring creases, marks and traces of stacking on the inner surface. The black colour is not uniform and frequently iridescent, with bubbles and burning traces on the external surfaces. These overall observations point at a poor control of the firing step conditions. The shapes of the objects do not allow recognizing particularly original products, but they are sufficiently comparable with pieces from analogous sites in *Magna Graecia* and Sicily [26]–[35]. They are mainly open shapes – plates and *patere*, or *paterette*, and *vasi potori*, cups and small cups – for daily use.

The archaeological macroscopic evaluation of the sample set identified three classes, mainly on the basis of the paste chromatic characteristics and on the inclusion frequency and features. For the present study, an adequate number of samples from each of the three classes was selected taking into account the representativeness of the various shapes (Table 1).

3. Methods

In order to perform SEM-EDS analyses the samples were embedded into acrylic resin. Thin sections were obtained from the embedded samples, polished with diamond pastes 15, 9, 6, 3, 1 µm, with Al_2O_3 0.5 µm and coated with carbon, approximately 30 nm thick.

SEM-EDS data were acquired using a scanning electron microscope (JEOL JSM-IT300LV) equipped with an EDS Oxford Instruments X-Act SDD detector using the Energy 200 Inca Suite provided with Automate package version 4.14. Taking into consideration the inclusion size (usually between 20 and 100 µm length, with few exceptions up to 200 µm) of the analysed sherds, a 500 X magnification was chosen, corresponding to a Field of View (FOV) of 256x192 µm and pixel resolution=0.5 µm. EDS maps were acquired with a short pulse processing time constant, in order to achieve statistically significant counts also for a short dwell time. Under these conditions, using a modern Silicon Drift Detector (SDD) with counting frequencies greater than 100.000 counts/sec, a dwell time of 1 ms was selected, corresponding to an acquisition time of approximately 4h (1.4 x 10^9 total X-ray counts) for each sample. In the case of average matrix analysis, where the spectrum

of each field contains ≈ $5*10^7$ X-ray counts, the analytical precision is below 0.01 element Wt%. Each set of X-ray maps was corrected for the instrumental probe current drift due to the long acquisition times, by performing an automated measure on a Co reference sample of known (x, y, z) coordinates at a prefixed 1 hour time intervals. The accelerating voltage was set at 15 kV, the probe current at 2 nA and the working distance at 10 mm.

Full quantitative analysis used filtered least square treatment [36] and quantitative ZAF correction [37] (Inca Energy 200©, Suite version 4.14(2009)). Natural minerals from Astimex Scientific Limited® were adopted as standards (Albite (Na), Periclase (Mg), Almandine Garnet (Al and Fe), Quartz (Si), Apatite (P), Sanidine (K), Wollastonite (Ca), Rutile (Ti)).

The analytical protocol consists of 5 steps:

1) a regular grid of 20 maps, separated and homogeneously distributed on the thin section surface, was acquired for each sample. During map acquisition a data-cube file, containing a full EDS spectrum (0-10 KeV) for each X-ray map point, is stored for each sample. A thresholding process lead to the inclusion outlying;

2) each mineral inclusion quantitative chemical composition and morphological features were obtained and the data were stored in a database;

3) the database was processed by means of a hierarchical clustering algorithm. Each HCA cluster is identified as a specific mineralogical phase;

4) the corresponding mineralogical phase is assigned to each inclusion of each sample. The normative mineralogical distribution (expressed as total area %) is obtained for each sample;

5) the area corresponding to pores was determined and the matrix chemical composition was obtained (as sum spectrum of the overall area not associated to inclusions or pores).

Resulting data from step 4) and 5) was subjected to clustering to achieve fabric classification.

In order to confirm the obtained classification, the mineralogical composition of the ceramic sherds was checked by X-ray Powder Diffraction (XRPD) analyses and by OM investigations. XRPD evaluation was conducted on two representative samples while OM observation were conducted on the whole 22 sample set by an Olympus BX41 transmitted light polarizing microscope, coupled with a Jenoptick ProGres C5 digital camera, on the not graphitized thin sections.

XRPD patterns were collected by using an Analytical X'Pert Pro (PANanalytical B.V., Almelo, The Netherlands) equipped with an X'Celerator detector powder diffractometer using Cu Kα radiation generated at 45 kV and 40 mA. The 2θ range was from 5 to 90°. For the measurement, around 1 g of sample was ground in an agate mortar and the appropriate amount of powder (from both matrix and inclusions) was placed in a quartz sample holder and compressed with a glass slide. The X'Pert HighScore software was used for the evaluation of the diffraction patterns and the

identification of the mineralogical phases.

Agglomerative Hierarchical Cluster Analysis (HCA) was performed both on the mineralogical (inclusions) and chemical (matrices) datasets by the open access R [38] and the XLSTAT (Addinsoft Softwares) statistical software packages respectively, using Ward's method for building up dendrograms, after the autoscaling pre-processing procedure.

4. Results

The application of the analytical protocol on the 22 Adrano samples is exhaustively described in SM1. The results are illustrated in the present chapter.

4.1 Inclusions: outlining, mineral phase identification and chemical composition determination (step 1 to 3)

Resulting from step 1 to 3, ten inclusion mineral phases were detected in the overall examined ceramic corpus. The detected phases as reported in table 2 together with their chemical composition, expressed as cationic formula and their overall normative abundance (sum area %). The most abundant phase is quartz, as expected, corresponding to around 40 % of the total inclusions surface. Two different feldspars (K-feldspar and plagioclase) were distinguished, based on the stoichiometric relationships between the various cations, their abundance is 17 and 5%, respectively. As for the plagioclase, the cationic sum reported in Table 2 is lower with respect to the expected one, due to the fact that elements next to the detection limit, and/or showing high standard deviation, are not included in the formula. As a general statement, the matching between the theoretical and the obtained formula is directly related with the abundance of each phase, as can be deduced comparing Table 2 second and last columns. i.e. in the case of biotite (5% abundance) a sensible difference between the theoretical and detected K content (due to a very high standard deviation value) is observed, whereas in the muscovite the (Al, Fe) value is slightly lower than expected.

Moreover, two Ca-rich aluminosilicates were detected, one in higher abundance (ca. 20%) and the other with a frequency around 2%. Their formula was expressed based on the composition of the most similar petrographic group, i.e. the melilite group, and is indicated with 7 anions in Table 2 second column. Taking into account the considerations reported above, while the less abundant aluminosilicate could show a sizable deviation from the real stoichiometry, the other one represents a significant fraction of the total inclusion amount and its obtained composition is definitely consistent. In both cases, since the obtained stoichiometry partly diverges from the theoretical one

and given that the two minerals are probably neo-formation phases due to the firing process, they were generally indicated as Ca-aluminosilicate 1 (CaAlSil1) and Ca-aluminosilicate 2 (CaAlSil2). In more details, CaAlSi1 is characterized by higher Al and Si and lower Ca, while Fe and Mg contents are comparable.

Three further clusters were obtained, with abundance lower than 1%. Due to the consequent low precision, the composition of these three phases is not reported in Table 3. However, based on the overall evaluation of the cationic ratio, these phases were identified as apatite, calcium carbonate and iron oxides. In the case of iron oxides, the high compositional variability among the inclusions attests the presence in the group of both iron oxides and iron and titanium oxides. Due to the scarce relevance of these three phases, they were not considered for the classification of the samples discussed below.

The good concordance between the obtained stoichiometric formula with the corresponding reference formula for all the minerals present in significant abundance, demonstrates the suitability of the adopted procedure. On the other hand, the slight variability observed for muscovite and CaAlSil1 (see Figure SM4) can allow speculating on subtler differentiations (choosing a higher class number for the HCA).

4.2 Assignation of a mineralogical phase to each inclusion, acquisition of the normative mineralogical phase distribution and inclusions profile-based sample partition (step 4)

After phase identification, each outlined inclusion was associated to the mineralogical phase of the corresponding cluster (i.e. all the cluster 1 inclusions were identified as quartz), allowing to obtain the normative mineralogical distribution (expressed as total area %), of each phase in each sample, reported in Table 3 and Figure 5SM (step 4). These data were reported in bivariate diagrams in order to obtain the sample partition vs inclusions profile. For example, the diagram reported in Figure 1a, where the percentage of quartz + feldspars occurrence is projected vs. CaAlSil1 + CaAlSil2 content, allows to split the samples in two groups, named A and B (see also Table 3). A good negative correlation is estimable, with a less dispersed pattern for quartz-feldspars rich sherds (group A) with respect to a higher dispersion for the CaAlSil1 + CaAlSil2 rich samples (group B). In group A samples, quartz content is always above 50%, with the exception of the S16 and S19 samples (Table 3). Conversely, group B samples show a high CaAlSil1 + CaAlSil2 content, ranging from 30 to 60%. Finally, sample S05 falls between the two main groups due to its quartz vs. total CaAlSil contents (Figure 1b), very low plagioclase content and micas exceeding 20% (Table 3). Also S11 sample shows intermediate CaAlSil1 + CaAlSil2 and quartz concentrations (Figure 1b) and places between the two groups.

XRPD analyses performed on two representative samples confirmed the overall mineralogical pattern identified by the proposed method for both groups (SM3 and Figure SM8).

4.3 Matrix chemical composition (step 5)

Pores were identified by using the Oxygen X-ray map selecting a threshold value in 0-10 grey level range. Matrix was obtained as the whole sample surface not occupied by inclusions and pores.

Matrix average EDS chemical compositions (and the corresponding standard deviations) are reported in Table SM2, expressed as wt% of the oxide contents.

The SiO_2 vs. CaO (Figure 2a) bivariate diagram illustrates the presence of two groups, a first one (almost corresponding to group A from petrographic analyses), characterized by high SiO_2 (from 57 to 62 Wt%) and low CaO (from 7 to 13 Wt%) contents, and a second group (almost corresponding to group B from petrographic analyses), characterized by higher CaO (from 17 to 24 Wt%) values, and lower SiO_2 (from 49 to 55 Wt%) abundances. Few samples fall at the boundaries of the two groups: samples S14 and S20, characterized by intermediate contents of both SiO_2 and CaO. A similar grouping can also be deduced from the diagram (Al_2O_3 + Fe_2O_3) vs. CaO, where a good linear anti-correlation is evident (Figure 2b). Also in this case sample S20, together with S11 and S19, plots in an intermediate zone of the diagram.

As a general statement, from the matrix chemical composition it can be deduced that group A, characterized by lower CaO abundance, is essentially clayey, whereas the matrix of group B, rich in CaO, has a marly nature. This difference can be attributed to distinct raw materials that, following the technological process, provided different firing products: the development of an isotropic matrix for the first group, poor in lime, and of Ca-aluminosilicates formed after reaction between the carbonate fraction and the clay minerals for the second group, generally suggesting firing temperatures higher than 850°C. [39]–[41]

5. Discussion

When chemical and mineralogical data are ~~considering~~ considered together, plotting the inclusion mineralogical profile (quartz-feldspars rich vs Ca-aluminosilicates rich samples Qz+Pl+Kfs/Qz+Pl+Kfs+CaAlsil1and2) vs the matrix chemical profile (SiO_2/SiO_2+CaO, i.e. more siliceous or more carbonatic matrix) (Figure 3) the group A and B classification is confirmed, with samples S05 and S11 falling in an area between the two main groups, confirming their transitional characteristics for both inclusion and matrix compositions.

By jointly subjecting both datasets to HCA clustering method the two main classes are confirmed, with an additional partition of group A in two subclasses (Figure 4).

The comparison of the results obtained with the proposed procedure with those arising from the traditional OM observation (Table 4, line 3) confirms that the two approaches lead to the same partition, but the first method provides further and subtler information. In particular, the evaluation of the data obtained by the proposed automated procedure by considering only the inclusion mineral-chemical composition highlighted the presence of four peculiar samples, namely S5, S11, S16 and S19 (Table 4, line 1). When both the inclusion mineral-chemical composition and the matrix chemical composition are considered (Table 4, line 2), one out of the four samples (S16) is reassigned to group A, but the other three samples cluster together in a subgroup (A2), as also evidenced in Figure 4.

Moreover, the proposed approach allows to automatically and quantitatively evaluate the mineralogical and chemical characteristics of these peculiar samples. This is an important issue, since peculiar samples and/or outliers are usually very significant in the evaluation of the technological dynamics of a specific archaeological site, i.e. peculiarities can be either indicative of further differentiation (e.g. between workshops), or simply due to a scarce standardization or to a different provenance. In more detail, if a different provenance can be excluded for the peculiar samples, their characteristics and their attribution to different ateliers of a same site could give important information on the number and type of ceramic workshops, on their evolution over time, on their eventual specialization in a specific ceramic typology. However, a greater number of samples would be necessary for a better statistical evaluation and would help to give a deeper explanation of these variations for the examined Adrano ceramic *corpus*. Notwithstanding some considerations can be carried out.

When comparing the obtained classification with the results emerging from the autoptic observation only a partial correspondence can be observed. The correspondence between archaeological classes I-III and groups A and B obtained with the proposed method is slightly different, depending on the considered dataset (chemical, mineralogical or both). When chemical and mineralogical dataset are considered together Class 1 (Table 1) can be partly connected to group A, with the exception of samples S09, S10 and S11 and the samples attributed to class 2 are distributed in both group A and B. Thus, the differentiation between red (Class 1) and yellow (Class 2) pastes should not be ascribable to a stylistic choice, being imputable only to the firing conditions. Finally, class 3 grey samples are split in group A and B, indicating that also in this case the resulting color was not due to a specific selection of the raw materials, but rather either to an intentional technological choice by using reducing conditions during the firing step or to a limited ability in controlling the kiln atmosphere.

Comparing the partition obtained with the proposed method with previous publications on Adrano pottery, the classification in two main compositional groups partially resembles the results already reported by Aquilia [42] on a set of 28 kiln wastes from Adrano. In the present case, no raw material reference sample is available to advance hypothesis about the location of the areas of origin of the sherds, but it can be assumed that quartz rich samples are compatible with the Terravecchia Formation [42]. On the other hand, the hypothesis that all the samples are of local origin is plausible due to the geological complexity of the area and supported by the recovery of numerous kiln wastes, whose chemical composition [43] spread the samples on both the observed classes.

As a general statement, in situations where reference materials are available, also a provenance evaluation could be carried out, with a sophisticated approach. Indeed slight differences in the cationic composition within the individual mineralogical phases are also appreciable. For example, in the muscovite histogram, the correlation between the increase in silicon content and the decrease in aluminum content can be observed due to the partial replacement of muscovite by phengite, the corresponding high pressure di-octahedral mica (Figure SM4). Analogously, in the biotite diagram (not showed) the cationic substitution between Fe and Mg is evident.

These observations can give an important contribution to the formulation of hypotheses related to the origin of raw materials used in the production of ceramics. Muscovite is a typical mineral of medium-grade and low-pressure metamorphic rocks or even granite rocks, while phengite forms only in metamorphic high-pressure rocks, which have undergone a subduction event. Therefore, comparison of mineralogical data with the knowledge of regional geology could allow constraining the sites of raw material exploitation.

Finally, although the morphometric features have not been used for classification purposes in the present work, the graphs related to shape, Aspect-ratio and ECD for CaAlSil1 and K-feldspar reported in Figure SM7 show a difference between A and B classes, according to the ascertained partition highlighting that also the morphometric dataset could be used to obtain sample partition.

5. Conclusions

This paper presents a new analytical protocol for the ancient ceramics *fabrics* identification and classification, based on a SEM-EDS X-ray maps acquisition and constituting an improvement to the usual archaeometric procedure of observing ceramic inclusions by OM and determining the chemical matrix composition by SEM-EDS.

Indeed, using the proposed procedure the quantitative mineralogical pattern and the chemical

composition of both mineralogical phases and matrix can be simultaneously determined. Inclusion morphological parameters can also be obtained and eventually used with classification purposes. Slight differences in the cationic composition within the individual mineralogical phases are detected, eventually allowing to perform provenance evaluations, comparing diagnostic features with geological samples. Moreover, the data acquisition is an automated procedure, not depending on the operator intervention. Finally, matrix analysis is conducted on the whole analysed area, which is statistically very relevant, leading to a precision below 0.01 element Wt%.

In the present work the proposed procedure was applied to an archaeological ceramic *corpus* but the method could be fruitfully used on various heterogeneous/composite materials.

The application of the proposed procedure on 22 samples from Adrano (NE Sicily) demonstrates that the samples can be efficiently partitioned with this method, as confirmed by the classic thin section OM petrographic observation but, when both mineral (inclusions) and elemental (matrix) datasets are considered together, the proposed procedure shows a subtler classification power, allowing to distinguish slightly peculiar samples. XRPD further confirms that the recognition of the most abundant phases is reliable and, based on the mineralogical patterns observed for both groups, suggests the use of original firing temperatures from 850°C up.

From an archaeological point of view, the results of the present paper did not evidence the predominance of a specific *fabric*. Moreover, the classification of the black glazed Adrano pottery in two main *fabric* mirror the results obtained in previous studies but, the proposed procedure evidences the further presence of few peculiar samples that can be informative of the evolution and the dynamics of the ceramic production in the archaeological site, i.e. differentiation vs the object shapes between workshops or scarce standardization. A higher number of samples would allow a deeper statistical evaluation and probably would help to better attest for these variations. This in-depth analysis on the Adrano ceramic materials would be particularly recommended, since the autoptic examination results corresponded only partially to the classification based on the archaeometric data.

Acknowledgments

The authors would like to acknowledge Dr. Umberto Spigo for his liberality in allowing young scholars to explore the archaeological research in Adrano, for continuous dialogue, discussion and support. We would also like to thank Prof. Ciaran Ward for his valuable linguistic advice concerning the material description. This research has been supported by Italian Ministry of University and Research (Grant Ricerca Locale ex60% 2014-2015).

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Tables:

Table 1: Macroscopic description of the 22 analyzed samples. The fragments are identified by a sequential inventory number, preceded by an acronym indicating the specific location of the discovery (BA = *Proprietà Battiati*, BE = *Proprietà Bertolo*, BM = *Proprietà Bandieramonte*, DLS = *Proprietà Diolosà*, DV = *Piazza Dionigi il Vecchio*, ZP = *Proprietà Zappalà (Puleo)*).

Table 2: Detected inclusions mean cationic composition of each cluster identified by HCA expressed on 8 anions (first column), corresponding cationic formula expressed on the appropriate number of anions (second column), reference formula (third column) and inferred mineral (last column). Last column: total abundance (Area%).

Table 3: Normative mineralogical composition of the inclusions for each sample (expressed as Area %, n.d.= not detected) and resulting classification in group A and group B.

Table 4: Comparison of obtained classification (data from Figura 4, Table 3 e supplementary materials SM2-OM). ( ) = peculiar sample from inclusion dataset evaluation.

Figures:

Figure 1: a: Bivariate diagram of quartz + feldspars sum vs. total CaAlSil1+CaAlSil2 (Area %); b: Bivariate diagram of total CaAlSil1+CaAlSil2 vs. quartz contents (Area %).

Figure 2: a: Bivariate diagram of SiO_2 vs. CaO matrix content (Wt%); b: Bivariate diagram of Al_2O_3+Fe_2O_3 vs. CaO matrix content (Wt%).

Figure 3: Bivariate diagram of mineralogical distribution ((quartz+plagioclase+K-feldspar)/(quartz+plagioclase+K-feldspar+ CaAlSil1+CaAlSil2), area %) vs. matrix chemical ratio SiO_2/(SiO_2+CaO) (Wt%).

Figure 4: HCA dendrogram (Ward) obtained from the whole mineral-chemical (inclusions) and chemical (matrix) composition, expressed as oxides Wt%.